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THERMAL DEHYDRATION OF $(C_6H_5-NH_3)_4Mo_8O_{26} \cdot 2\ H_2O$. ISOTHERMAL KINETIC ANALYSIS

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ABSTRACT

The thermal dehydration of $(C_6H_5-NH_3)_4Mo_8O_{26} \cdot 2\ H_2O$ in powder and pellet form has been studied by thermogravimetry.

The dehydration takes place as first reaction for the isothermal and non-isothermal runs. In the powder samples the final mass loss of water gives a non-stoichiometric amount near 3/2 H_2O. A stoichiometric decomposition takes place in the pellet samples. Non-stoichiometric runs are explained as a result of premature pore closure at the surface of the reacting particles, by the influence of structural effects in the dehydration, which can be avoided in the pellet runs.

The reaction kinetic model of the isothermal dehydration between 348 and 373 K was found to be the topo-chemical KEKAM equation and the temperature was found to have an influence on the limiting stages of the transformation $1 < n < 3/2$.

The values of the frequency factor and activation energy were $A = 2.93 \times 10^{13}$ min^{-1} and $E = 101.20$ kJ mol^{-1}, respectively.

INTRODUCTION

Although the thermal decomposition of ammonium and nitrogen organic derivatives polymetalates has been studied extensively in order to describe the thermal behavior of this kind of compounds [1-14] as well as for their application as specific materials for industrial purposes [15], kinetic studies have been scarcely reported. In both topics it is very important to know in detail the different steps of the thermal decomposition. It is known that this kind of compounds has two decomposition steps. First, the dehydration takes place between approximately 348 and 443 K and second, the polymetalato decomposition takes place from 473 to 773 K.

Schwing-Weill gives a dehydration reaction with more than one step for the pyridium tetramolybdate monohydrate [16] and for the piperidinium tetramolybdate dihydrate [3] and these different steps are explained with some intermediate hydrates.

The isothermal and non-isothermal study of the thermal decomposition of the anilinium octamolybdate dihydrate shows that the final mass loss is non-stoichiometric in the powder samples but is stoichiometric with pellets obtained from the powder sample, so that the partial loss of water can be explained by structural effects in the solid matrix, which can be avoided by pelletization at 5 atm of pressure.

This paper is a study of the thermal dehydration of $(C_6H_5-NH_3)_4Mo_8O_{26} \cdot 2\ H_2O$ by means of thermogravimetry in isothermal runs. Basic kinetic constants such as the kinetic model, pre-exponential factor, and activation energy were determined.

EXPERIMENTAL

Materials

Anilinium octamolybdate was prepared for the first time in our laboratories by the reaction of aniline (99.9%, Merck) and molybdenum trioxide in aqueous solution at pH 2.8. After crystallization and purification, X-ray and infrared characterizations were made. Experimental processes and characterization data are described in ref. 17.

Analysis: found (%): C, 18.20; H, 2.24; N, 3.62; calc. (%): C, 18.06; H, 2.27; N, 3.51.

Measurements

The product was pulverized with a mortar and pestle and sieved to a narrow fraction of 150–200 μ in order to carry out the dehydration process under the same condition for all the samples. Cylindrical pellets were made from the powder using a Perkin-Elmer (P/N 15.010) hydraulic press at 5 atm of pressure.

The isothermal and non-isothermal TG curves were recorded on a Perkin-Elmer TGS-1 with a dry nitrogen flux of 50 ml min^{-1}. About 5 mg of sample were weighed into an aluminum crucible and measured by use of a reference material.

RESULTS AND DISCUSSION

The compounds studied presents a three-step decomposition pattern, leading to a residual weight equal to that expected for MoO_3 in the non-isothermal runs (Fig. 1).

In recent years Criado and Morales [18,19], and several others workers have pointed out that the reaction mechanism could not be deduced from a single TG diagram.

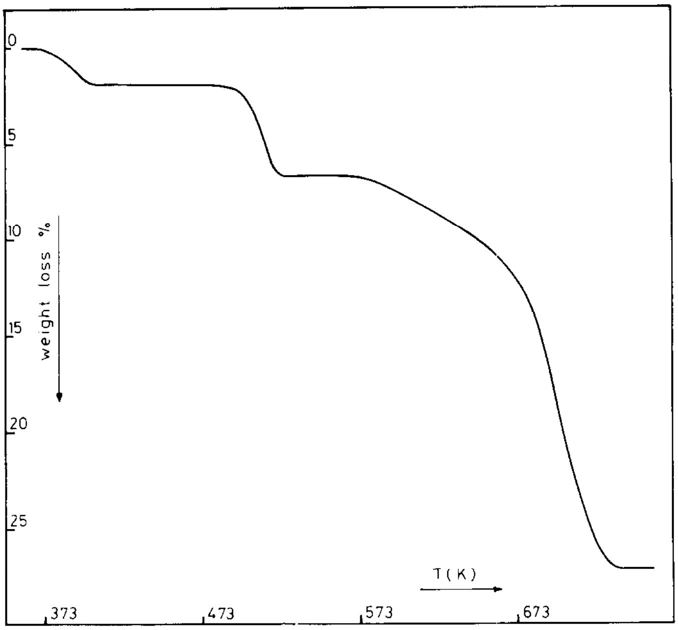

Fig. 1. Non-isothermal decomposition of $(C_6H_5-NH_3)_4Mo_8O_{26}\cdot 2\ H_2O$ at a heating rate of 10°C min^{-1}.

For the above reason the dehydration reaction was studied in more detail under isothermal conditions, between 348 and 373 K with a heating rate of 360°C min^{-1} for a period of time in order to avoid the artificial induction

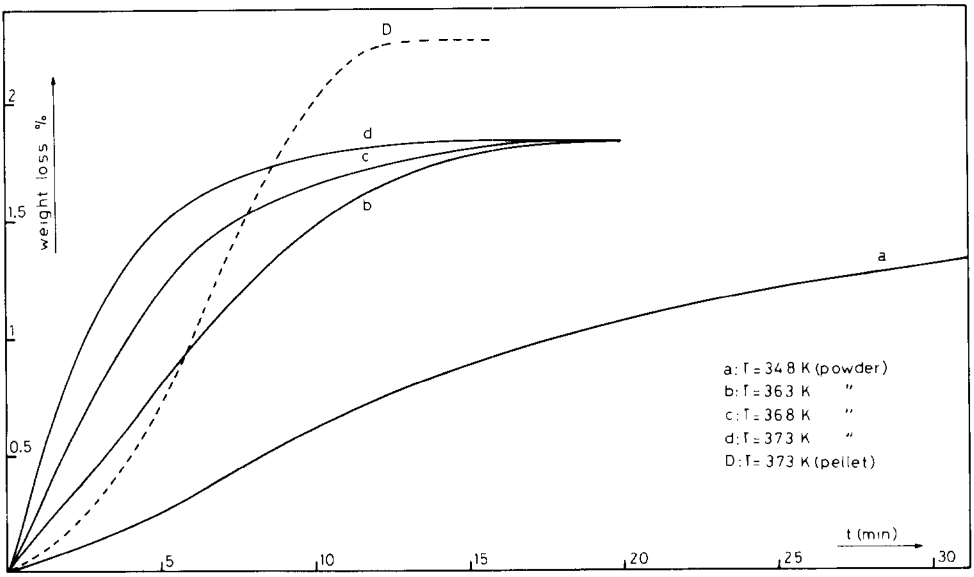

Fig. 2. Isothermal decomposition of $(C_6H_5-NH_3)_4Mo_8O_{26}\cdot 2\ H_2O$ between 348 and 373 K. (———) Powder samples, (— — —) pellet samples.

TABLE 1

Final weight loss at different temperatures for powder and pellet samples

T(K)	Final weight loss (%)
348	1.78
363	1.80
368	1.79
373	1.85
373 (pellets)	2.2
400 (non-isothermal)	1.95

and acceleratory periods. The weight loss percentages for the powder samples (solid curves) and for the pellet sample (broken lines) are shown in Fig. 2.

The elemental analysis of the samples after the first decomposition step shows that the mass loss is only of water.

Isothermal and non-isothermal runs of the powder samples show a partial loss of water (Table 1) and this is a constant value near 3/2 H_2O. This partial loss of water can be explained in two different ways, firstly, it can be supposed that some intermediate hydrates are obtained in the thermal decomposition [3,16] or secondly, that the incomplete conversion is a result of premature pore closure at the surface of the reacting particles [20, 21]. From the X-ray diffraction pattern of the powder samples it is impossible to know if a new hydrate is formed; the results are practically the same for the two samples. The influence of structural effects in the dehydration can alternatively be shown as in Fig. 2 and Table 1. The final mass loss for the dehydration of a pellet, obtained from the powder at 5 atm of pressure is always a stoichiometric amount (2 H_2O). From these results the partial loss of water is explained by structural effects and it can be said that different salt properties, like porosity or geometrical characteristics, which can be changed in the pelletization operation have a very important influence on the final mass loss of the dehydration step.

In order to analyze the α–t curves, ten different kinetic models (shown in Table 2), have been fitted by least squares. A least squares fit for the different models is shown in Table 3. In this table it can be seen that the best fitting is for the KEKAM (Kolmogorov–Erofeev–Kazeev–Avrami–Mampel) equation [22]. This is the well-known topochemical equation, which is of particular interest for kinetic analyses aiming to determine the value of the exponent n, which allows the limiting stages of the transformation to be found.

The first observation of the kinetic model is the influence of the temperature on the exponent n of the equation. The limiting stages of the transformation are a function of the temperature, as shown in Fig. 3. At low

TABLE 2

Kinetic models

Kinetic model	f(α)	g(α)	
1. Nucleation and nucleus growing (Kolmogorov–Erofeev–Kazeev–Avrami–Mampel, KEKAM, equation)	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{1-n}$	1. $[-\ln(1-\alpha)]^n$	
2. Phase boundary reaction	$(1-\alpha)^{1-1/F_p}$	2.1. $1-(1-\alpha)$	Plane symmetry
		2.2. $1-(1-\alpha)^{1/2}$	cylindrical symmetry
		2.3. $1-(1-\alpha)^{1/3}$	spherical symmetry
3. Diffusion	3.1. α^{-1}	3.1. α^2	plane symmetry
	3.2. $[-\ln(1-\alpha)]^{-1}$	3.2. $(1-\alpha)\ln(1-\alpha)+\alpha$	cylindrical symmetry
	3.3. $[(1-\alpha)^{1/3}-1]^{-1}$	3.3. $3/2\ (1-2/3)\alpha-(1-\alpha)^{2/3}$	spherical symmetry
4. Potential law	$1/n\ \alpha^{1-n}$	4. $\alpha^n\ (0 < n < 2)$	
5. Reaction order	$1/n(1-\alpha)^{1-n}$	5.1. $1-(1-\alpha)^2$	order 2
		5.2. $1-(1-\alpha)^3$	order 3

TABLE 3

Least squares fit for the different models of Table 2

T(K)	1			2.1		2.2		2.3		3.1	
	n	$\ln K$	r^2	$\phi_1 K$	r^2	$\phi_1 K$	r^2	$\phi_1 K$	r^2	$\phi_D D_e$	r^2
348	1.12	$-.743$	0.996	0.00958	0.983	0.01178	0.989	0.01402	0.928	0.00371	0.909
363	1.28	-2.406	0.994	0.03409	0.982	0.04131	0.952	0.04757	0.788	0.01348	0.962
368	1.33	-1.870	0.996	0.09833	0.919	0.12068	0.958	0.14086	0.984	0.03921	0.810
373	1.37	-1.409	0.996	0.10891	0.984	0.13789	0.972	0.17364	0.906	0.04065	0.960

T(K)	3.2		3.3		4			5.1		5.2	
	$\phi_D D_e$	r^2	$\phi_D D_e$	r^2	n	$-\ln K$	r^2	K	r^2	K	r^2
348	0.01314	0.948	0.01531	0.987	1.28	4.05	0.948	0.01273	0.697	0.01056	0.531
363	0.04691	0.972	0.05290	0.945	1.20	2.72	0.943	0.04224	0.484	0.03540	0.328
368	0.13955	0.868	0.16191	0.959	1.06	1.88	0.988	0.11981	0.810	0.09280	0.619
373	0.14936	0.968	0.18306	0.966	1.02	1.59	0.952	0.16421	0.722	0.13829	0.564

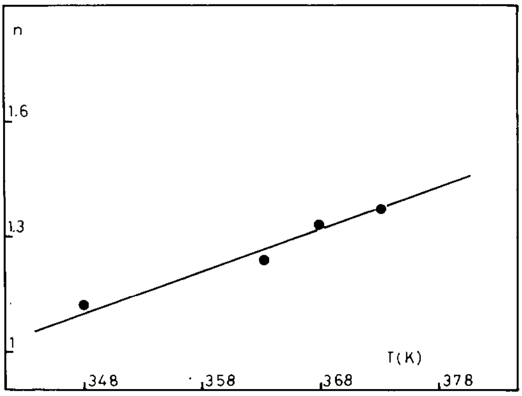

Fig. 3. Dependence of the limiting stages of the transformation *n* on the temperature.

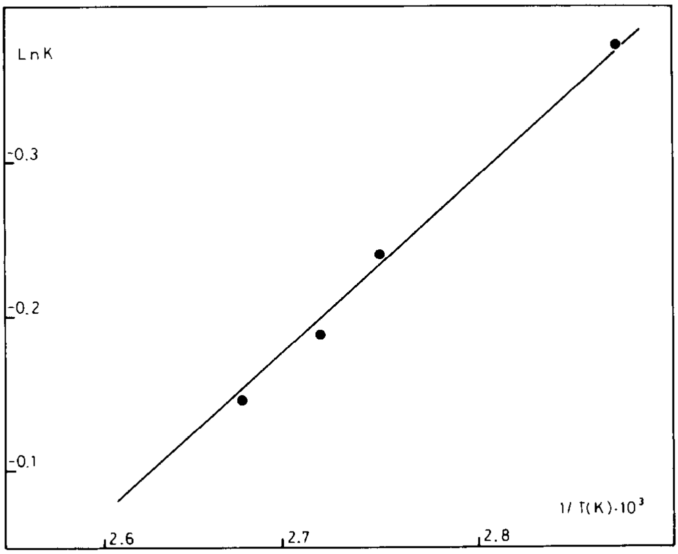

Fig. 4. Arrhenius plot of the kinetic parameters obtained from the KEKAM equation.

temperature *n* approaches 1 and at higher temperatures *n* reaches 1.5.

The Arrhenius plot to obtain the pre-exponential factor and the activation energy is shown in Fig. 4. The correlation coefficient for the least squares fit $r^2 = 0.998$; the pre-exponential factor $A = 2.93 \times 10^{13}$ min^{-1} and the activation energy $E = 101.20$ kJ mol^{-1}.

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